DYNAMICS OF HEAVY METALS MIGRATION IN THE SOIL AS A CONSEQUENCE OF MILITARY ACTIONS

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Abstract. The military operations in Ukraine have consequences for the biosphere, which is negatively affected by the hostilities, causing its destruction and degradation, – soils. It is currently impossible to fully assess the impact of military and terrorist actions on the environment due to the lack of accurate information. The shelling of civilian and strategically important objects in Ukraine created synergistic conditions for the environment to accumulate and enter through leaching from the soil a large amount of heavy metals into surface water. Accordingly, this leads to mass degradation of not only the soil environment, but also the hydrosphere and plant life. The entry of potentially toxic elements (PTE) into the environment, soil and plants is accompanied by their oxidation and other chemical processes. Soil sampling was carried out by the method of a concentric circle, in the canter of which is the source of pollution, which allows us to assess the degree of distribution of potentially toxic elements depending on the depth of the well. In our research on the content of heavy metals in the soil during the shelling of Lviv and 6 months later, XRF and ICP analyzes of soil samples. The results of the analysis of the content of heavy metals in the soil after 6 months show that the concentration of cadmium is reduced by two times; copper and nickel, respectively, 3 and 3.5 times; lead+ and chromium – twice. It is known that heavy metals do not undergo decomposition processes, but can only be redistributed between natural environments. They tend to concentrate in living organisms, causing various pathologies.

Keywords: military affected area, heavy metals; soil pollution, plants, migration of heavy metals in the soil.

1. Introduction

The military operations in Ukraine have consequences for the biosphere, which is negatively affected by the hostilities, causing its destruction and degradation, – soils. It is currently impossible to fully assess the environmental impact of military and terrorist actions due to the lack of accurate information.

The detonation of munitions can have a negative impact on the environment, which leads to soil, water and air pollution. During the detonation of military missiles, artillery shells, mines, a number of chemical compounds are formed: carbon monoxide, carbon dioxide, water vapor, brown gas, nitrogen, etc.

During the explosion, all substances are completely oxidized, and the products of the chemical reaction are released into the atmosphere. Additionally, a large amount of toxic organic matter is formed, and the surrounding soil, wood, and structures are oxidized. Then there are also a number of toxic elements, such as oxides of sulfur and nitrogen, which during oxidation can lead to acid rain. They can change the pH of the soil, cause burns to plants, mucous membranes of the respiratory organs of humans, birds, mammals, and so on. However, it is not the detonation of shells that poses a greater risk to the environment, but rather hits to industrial or chemical facilities.

As a result, shelling can pollute not only air and soil, but also groundwater. And since agricultural products can be grown on the soil and groundwater can be used as a source of drinking water, all these elements can enter the food chain. And if they get into the human body, this can lead to significant health problems in the future.

The metal fragments of shells that get into the environment are also not safe and completely inert. Cast iron with steel impurities is the most common material for the production of ammunition casings and contains not only standard iron and carbon, but also sulphur and copper. These substances get into the soil and can migrate to groundwater and eventually enter the food chain, affecting both animals and humans (Battsengel et al., 2020).

A separate danger is the mining of fields – soil contamination can lead to the fact that it will not be possible to grow anything in these territories for some time. Now, according to the UN, Ukraine is one of the most mined countries in the world. Almost 15 % of the total area is mined. This will directly affect soil pollution. Demining of this territory or detonation of mines will also lead to heavy metal contamination of soil and groundwater. In addition to oxidation during the explosion, projectile fragments that enter the environment are dangerous. They contain impurities of cast iron, iron, carbon, sulfur and copper, which can lead to soil and underground water pollution.

The fuel that can remain in the rocket after "arrival" is also dangerous. A missile that has a range of, for example, 5,000 km, but has flown a thousand, is fully fueled. That is, it still remains in the rocket during impact. These oil products pollute land resources. And this is confirmed already by the first results of the analyses. In addition, munitions explosions can contribute to further climate change. During the explosion, greenhouse gases are released – this is carbon, water vapor. They are not toxic, but directly affect climate change.

On a smaller scale (but with a greater variety of impacts), the source of pollution is also burnt tanks, vehicles, downed planes and other remnants of hostilities. Military equipment has the same effect as shell fragments. That is, metal impurities can pollute soil and underground water. Plus, military equipment has a lot of fuel, which leads to burning, air pollution, and potentially soil and water pollution. Getting equipment into rivers and lakes is also dangerous, because metal oxidation can lead to water pollution (Certinet et al., 2013).

Soil contamination with fuel and lubricants and other petroleum products occurs as a result of the movement and damage of ground military equipment. In soils impregnated with fuel and lubricants, water permeability decreases, oxygen is displaced, and biochemical and microbiological processes are disrupted. As a result, the water and air regimes and the circulation of nutrients deteriorate, the root nutrition of plants is disturbed, their growth and development are inhibited, which causes death.

2. Materials and Methods

The multielement composition was estimated by the ICP-OES method (ICP-OES Varian Vista-MPX, Australia). The analysis was carried out separately for each soil sample with full compensation for matrix effects, taking into account the principles of measurement traceability. This method of soil sampling provides the following information: the concentration of substances in the explosion centre; the distribution of soil contamination depending on the depth of the crater; and the form of contamination spread.

Inductively coupled plasma atomic emission spectroscopy (ICP-OES), also known as optical emission spectroscopy with inductively coupled plasma, is an analytical technique used to detect chemical elements. It is a type of emission spectroscopy that uses an inductively coupled plasma to create excited atoms and ions that emit electromagnetic radiation at wavelengths specific to a particular element. The plasma is a high-temperature source of ionised source gas (often argon). The plasma is maintained by inductive coupling of electrical coils at megahertz frequencies. The intensity of the emission of different wavelengths of light is proportional to the concentrations of elements in the sample.

ICP-OES consists of two parts: an ICP and an optical spectrometer. The ICP burner consists of 3 concentric tubes made of quartz glass. The output or "work" coil of the radio frequency (RF) generator surrounds part of this quartz torch. Argon gas is usually used to create plasma. ICPs have two modes of operation, called capacitive (E) mode with low plasma density and inductive (H) mode with high plasma density, and the transition from heating mode E to H is done by external inputs. The burner works in H mode (Hassler, Perzl, 2003).

The sample solution is fed by a peristaltic pump through a nebuliser into the atomisation chamber. The resulting aerosol is converted into argon plasma. Plasma is the fourth state of matter, after the solid, liquid and gaseous states. In ICP-OES, the plasma is generated at the end of a quart torch using a cooled induction coil through which a high-frequency alternating current flows. As a result, an alternating magnetic field is induced, which accelerates the electrons to a circular trajectory. As a result of the collision between the argon atom and the electrons, ionisation occurs, forming a stable plasma. The plasma is extremely hot, 6000–7000 K. In the induction zone, it can

even reach 10000 K. In the torch, the sample is desolvated, atomised and ionised. Due to the thermal energy absorbed by the electrons, they reach a higher 'excited' state. When the electrons fall back to ground level, the energy is released as light (photons). Each element has its own characteristic emission spectrum, which is measured by a spectrometer. The intensity of the light at a wavelength is measured and converted into a concentration using a calibration (Zhang, Ma, 2002; Wiltsche, Wolfgang, 2020).

If the components of solid samples contain heavy metals, then the corresponding samples must first be identified and converted, i.e. liquefied, into a form suitable for ICP-OES analysis. This process is called digestion. It is carried out using microwave radiation, concentrated acids, and elevated temperatures and pressures in a special digestion apparatus. The process involves precise weighing of the sample material, quantitative transfer of the sample to the digestion vessels, careful addition of the concentrated acids required for digestion (mainly nitric acid, but also hydrochloric acid, hydrofluoric acid or mixtures), careful addition of the concentrated acids required for digestion, sealing of the vessels and their introduction into the digestion rotor. After digestion, the rotor with the vessels is removed and checked for damage. Only then are the digestion vessels removed and thoroughly ventilated in a fume hood to release any overpressure that may still be present. Otherwise, there is a danger to people and the environment due to the uncontrolled release of nitrous gases (Knut, Bernhard, 2016).

In the next step, the contents of the digestion vessels, consisting of the concentrated acids and the digested sample, are filtered and carefully transferred to volumetric flasks to avoid any sample loss that would lead to incorrect measurement results. The contents of the volumetric flasks are then filled to the mark with distilled water and thus prepared for measurement by ICP-OES (McClenathan et al., 2006).

The concentrated acid is then added back to the digestion flasks and the digestion procedure is carried out again as described, but without the sample. In this way, the digestion vessels are cleaned and prepared for the new digestion of the sample (Jantzi et al., 2016).

Before multielement composition assessment, soil samples were digested in a microwave digestion system (Start D, Milestone, Italy) using time and temperature programs (180 °C, 21 minutes). According to the following scheme, microwave excitation was carried out using ultrapure concentrated acids: 1. Soil samples (0.5 g) were treated with a diacid mixture of 7.5 ml of HCl and 2.5 ml of HNO_3; (2)

Samples of plant biomass from germination tests weighing about 0.5 g were digested with 5 mL of HNO_3 (Merck, Germany). After digestion, the solutions were filtered and diluted 100 times.

One of the main applications of inductively coupled plasma optical emission spectroscopy (ICP OES) is the analysis of elements at very low concentrations. If we consider such metals as mercury and arsenic, it is not difficult to understand the reason for these analyses. Soil sampling, food testing and drinking water analyzes are performed for human health and the environment, but the environmental sector is only one of the many important applications of ICP OES. Heavy metals have been polluting the environment for decades. Therefore, high-frequency tests with low detection limits have become the standard in many industries. Short analysis time, low sample preparation effort, multi-element detection and exceptional device sensitivity are the distinguishing features of this method. The latest generation of ICP OES devices makes elemental analysis even more convenient, economical and flexible (Merson, Evans, 2003).

The main stages of ICP metal analysis:

The elemental metals to be measured in the sample are selected. For example, iron (Fe), lead (Pb) and copper (Cu).

Sample solutions are prepared using generally accepted methods of quantitative chemical analysis.

A set of calibration solutions is prepared. Each solution contains precisely known concentrations of the analyte elements – Fe, Pb and Cu in this example. The concentration range for each element in the set is chosen to include the expected concentration of that element in the sample solutions (if known).

The next step in ICP metal analysis is to inject the calibration and sample solutions into the plasma and measure the light intensity on the respective analytical lines. For Fe, the emission wavelength can be 238.204 nm, for Pb 220.253 nm and for Cu 324.754 nm (Trevizan, Nobrega, 2007).

Calibration graphs are prepared for each element from the emission intensity of the calibration solutions.

The concentrations of the elements in each sample solution are determined from the calibration graphs. The concentrations in the original sample are then calculated based on the measured concentrations of the elements in the sample solution and a known dilution factor. ICP metal analysis provides results that contain the concentration of the selected elements, usually in µg/L or mg/L.
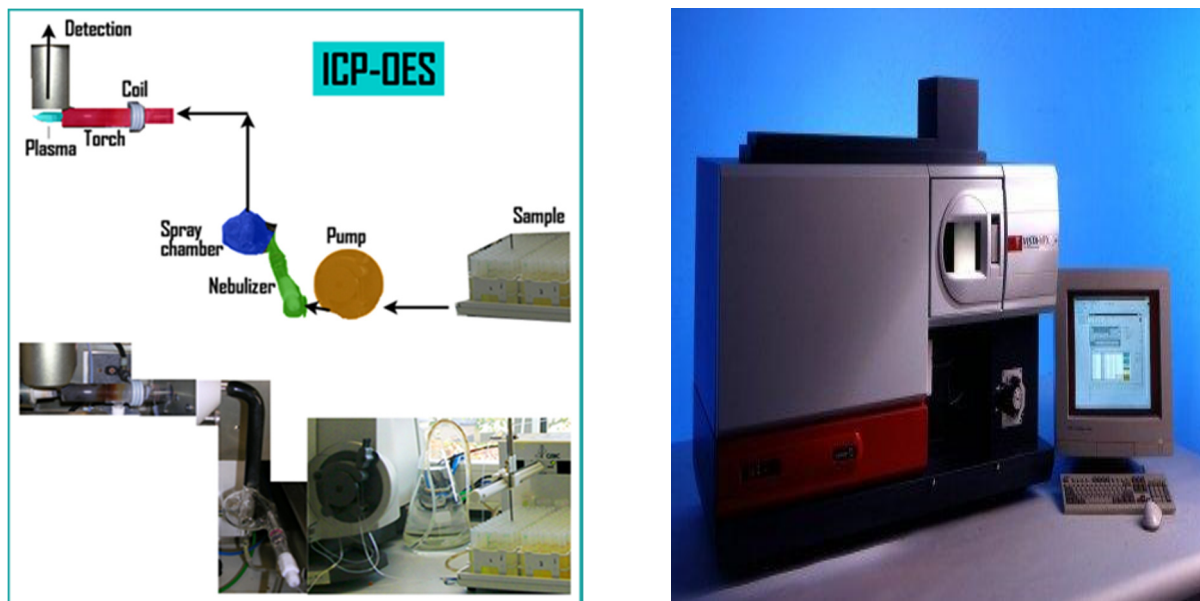
Fig. 1. The main stages of ICP OES analysis

3. Results and Discussion

The total content and descriptive statistics (minimum and maximum levels, as well as average values) for the six investigated heavy metals at the sites of the rocket explosion are given in the Table. 1.

The distribution of heavy metals in different soil samples showed spatial variations, which indicates the natural variability of the concentrations of these elements. The order of concentrations of the total content of elements in the studied samples is as follows: Cd > Cu > Pb > Cr > Zn > Ni.

Table 1

Total content and descriptive statistics of elements in soil samples by ICP-OES method (mg/kg)

Soil samples	Elements					
	Cd	Pb	Cu	Ni	Cr	Zn
G1	0.221	4	10.4	16.8	34.1	40.2
G2	0.112	7	19.1	18.1	19.1	21.8
G3	0.643	14.7	76.4	18.8	27.1	57.9
G4	0.4	25.1	12.3	16.9	34.1	77.6
G5	0.508	20.1	41.1	16.7	30.7	74.7
G6	0.076	24.1	30.3	20.1	30.7	83.5
G7	0.317	14.7	60.2	27	35.9	89.2
G8	0.048	35.1	75.7	25	35.5	124
G9	0.714	9.55	18.2	25.1	30.2	34.2
G10	0.367	12.7	56.2	24	33.2	75.5
G11	0.078	23.31	71.7	26	33.5	69.2
G12	0.925	21.41	28.2	25.1	32.2	98.43
MAC	20	3	10	50	100	23
Max	0.714	35.1	56.2	25.1	34.1	98.43
Min	0.076	4	12.3	16.8	19.1	21.8
Mean	0.367	17.648	41.657	21.638	31.358	70.519

Soil samples according to the designations G1–G3 – explosion site DI; G4–G6 – place of explosion of DII; G7–G9 – place of explosion DIII; G10–G12 – place of explosion DIV.

The obtained experimental data on the elemental composition of the studied soil in comparison with the standard for the permissible content of heavy metals in soil (Baraud et al., 2020; Taftazani et al., 2017; Trevizan, Nobrega, 2007) after missile strikes suggest a dangerous amount of elements such as lead (Pb), chromium (Cr), zinc (Zn), and nickel (Ni). Accordingly, if these elements are present in the soil,

they can form hazardous compounds that have an anthropogenic impact on the environment.

All soil samples showed an excess of maximum permissible concentrations of heavy metals. The most contaminated soil is that after the explosion in II and III districts (G7-9 and G10-12). All soil samples are characterised by a significant exceedance of the maximum permissible concentrations of such elements as titanium (two times), zinc (four times), copper (six times) and nickel (2.5 times), which is confirmed by experimental data obtained using the ICP-OES method (Fig. 2).

The results of analyzes of soil samples for heavy metals after the explosion indicate a significant excess of the maximum permissible concentrations for the following elements zinc (in samples G8-G12 – by three times); copper (in samples G7,10,11 – by 1.5–2 times); chromium (in samples G7,10,11 – by 0.5–1.6 times); cadmium (in samples G8 – by two times); lead (in samples G8-G10 – by ten times)), which is confirmed by the experimental data obtained. This creates a high risk of soil contami-

nation. Accordingly, this may contribute to the unpredictable nature of the environmental impact of the combination of the elements under study, since these heavy metals are not characterised by biodegradation, but rather by accumulation in the environment.

It should be noted that the relatively high content of titanium and zirconium in the soil samples is explained by the fact that these elements are the main components of the cruise missile body. Zirconium is used as an amplifier of strength and corrosion resistance of the cruise missile body.

The next stage of our research was to determine the residual concentrations of heavy metals in the soil after 6 months. This analysis of the concentrations of elements in the soil was carried out by XRF. For a more accurate reflection of the possibility of migration or accumulation of these elements in the soil, samples were taken at a depth of 1 metre from the soil surface at a distance of 1 metre and 5 metres from the centre of the explosion, respectively. A decrease in the concentration of heavy metals was observed in all soil samples.
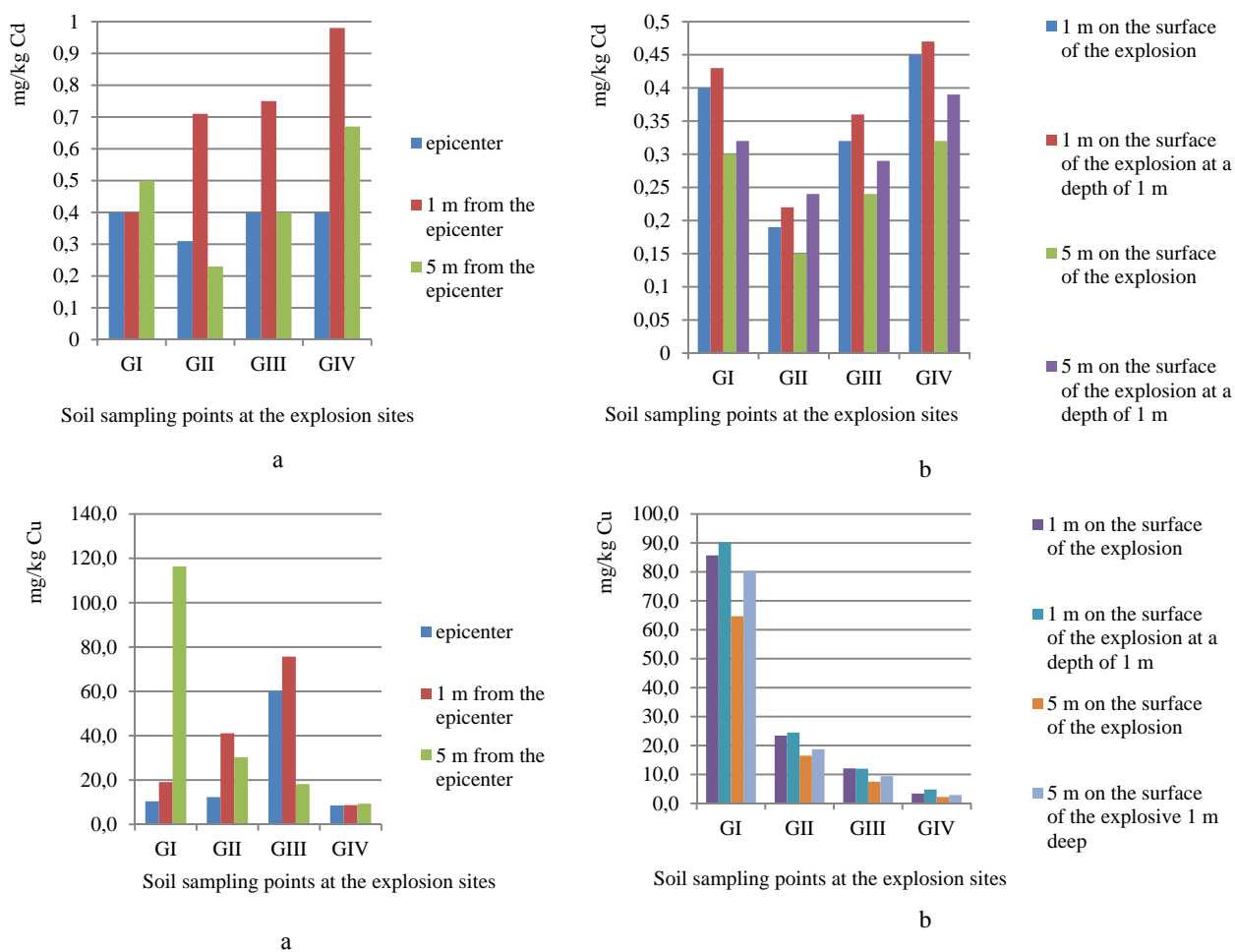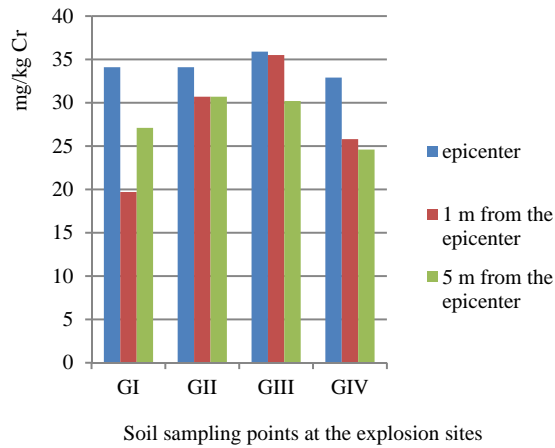

Fig. 2. Elemental distribution in soil samples:
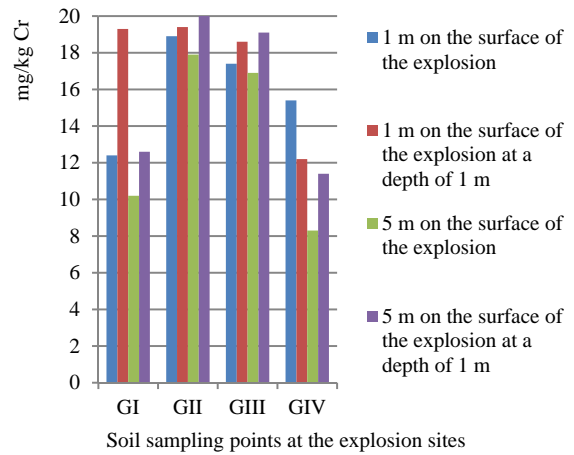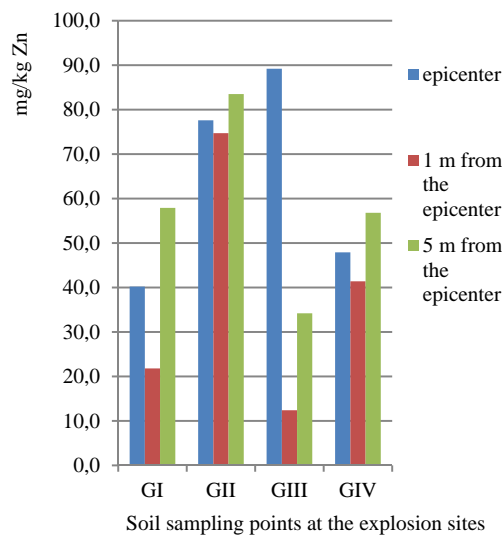a – analyzed ICP-OES; b – analyzed after 6 months by the XRF method
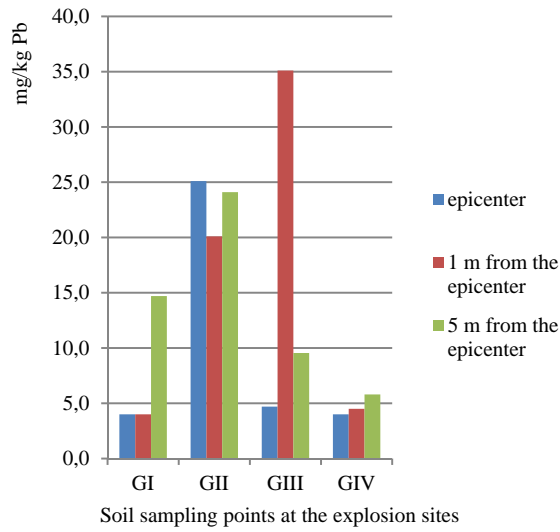
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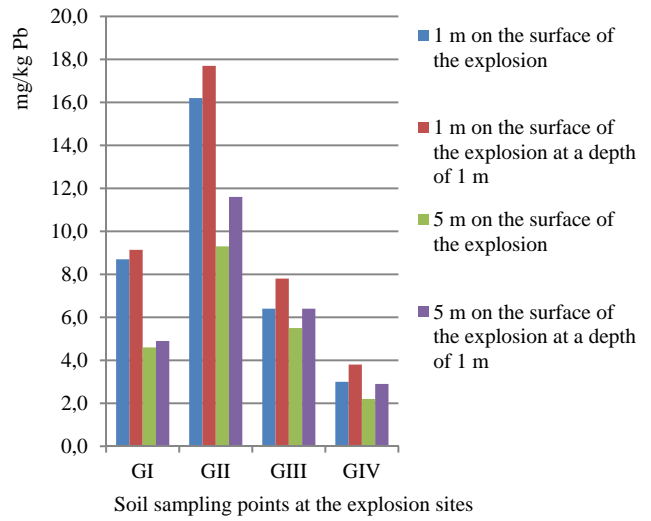
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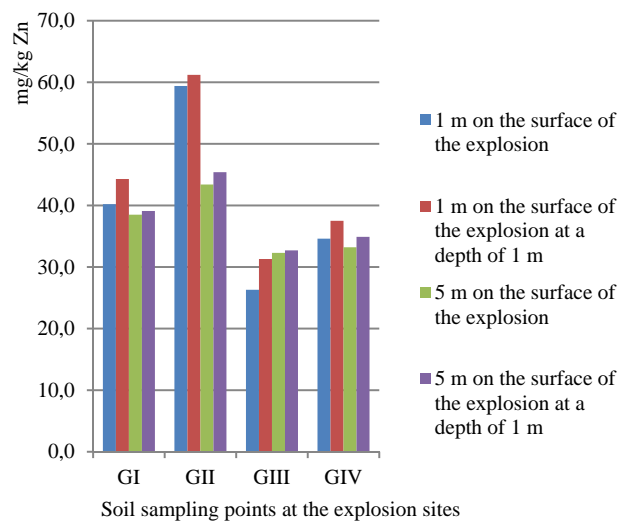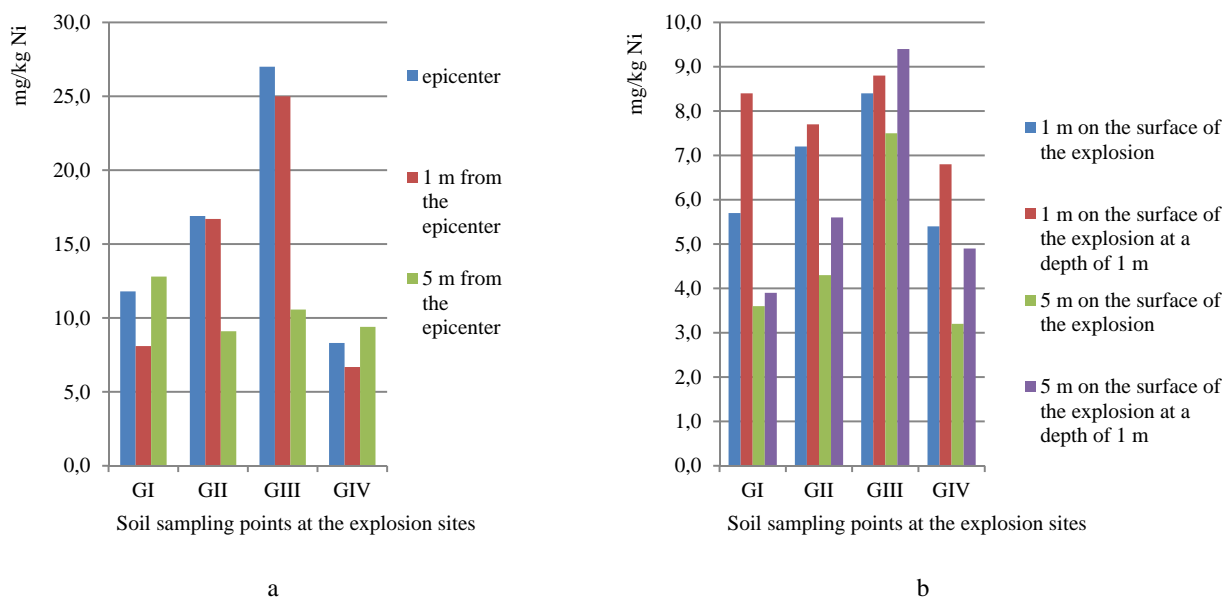

a

b

a

b

Fig. 2. (Continuation). Elemental distribution in soil samples:
a – analyzed ICP-OES; b – analyzed after 6 months by the XRF method

a   b

Fig. 2. (Continuation). Elemental distribution in soil samples:
a – analyzed ICP-OES; b – analyzed after 6 months by the XRF method

The results of the analysis of the content of heavy metals in the soil indicate that the concentration of cadmium is reduced by two times; copper and nickel, respectively, 3 and 3.5 times; lead and chromium – twice. It is known that heavy metals do not undergo decomposition processes, but can only be redistributed between natural environments. They tend to concentrate in living organisms, causing various pathologies. The results of our research indicate that most heavy metals are washed out of the soil and, accordingly, enter the surface water.

4. Conclusions

In the modern world, there were still no methods for calculating the damage to the environment from a war of this scale. As the war continues, we cannot know the full range and severity of its environmental effects, as data collection for further verification and assessment requires constant access. We can say with confidence that the thousands of already documented cases of soil, air and water pollution and deterioration of the ecosystem, unfortunately, will only increase.

We use optical emission spectrometry to analyze trace elements in soil samples from our experiments and field sites. ICP-OES measures the concentration of elements by exciting atoms in a sample with an inductively coupled plasma source and then detecting the emitted light at characteristic wavelengths. ICP-OES covers a wide range of elements, including metals and non-metals. It offers moderate resolution, allowing for the measurement of multiple elements simultaneously. ICP-OES typically has higher detection limits compared to ICP-MS, ranging from parts per million (ppm) to parts per billion (ppb). ICP-OES generally has higher sample throughput due to faster analysis times. It can analyze several samples per hour. ICP-OES is more susceptible to matrix effects and interference due to spectral overlap. Techniques such as background correction and standard addition can be used to mitigate these effects. ICP-OES is suitable for routine analysis of elements at higher concentrations in various industries such as environmental monitoring. ICP-OES is excellent for the rapid analysis of elements at high concentrations, making it suitable for routine analysis in various industries. For long-term studies of the impact of land use, species composition, tillage and fertilization on ecosystems in connection with climate change, elemental balance analysis is fundamental.

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